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Comparison of Calculated Excitation Rates with Spectral Intensities Measured in a Hollow Cathode

On the assumption that there is excitation only from the ground level by electron impact and only de-excitation by radiation, and by application of different distribution functions, the calculated intensity of the He-I singlet ($n^1D_2 - 2^1P_1$) and triplet ($n^3D - 2^3P$) systems are compared with intensities measured in a hollow cathode discharge.

The results showed that a much better fit between the calculated and measured values could be obtained by applying the Druyvesteyn velocity distribution of the electrons rather than the Maxwellian distribution. The greatest limitation of the applied model probably lies in neglecting the diffusion of neutral particles into the plasma.

Introduction

For the calculation of electron temperatures [1], excitation temperatures [1] and the density of electrons [2] or excited atoms [3] in a plasma, it is necessary to have an exact knowledge of the intensity values of distinct spectral lines. These values are determined spectroscopically.

Calculations can be done using certain equations and distribution functions (Saha, Boltzmann, Maxwell) [4]. The question is to what extent these expressions are valid in a hollow cathode discharge, because the plasma in the negative glow of a hollow cathode is not in a state of local thermal equilibrium (LTE).

This paper presents a comparison of measured and calculated values of intensities in order to determine whether the accepted equations are valid also in the case of a gas discharge in a hollow cathode.

Measurement of intensities

The intensities of some He-I spectral lines in a high current hollow cathode discharge [5] at a discharge pressure of $p = 1$ Tr and a discharge current of $i = 800$ mA were measured by means of a Steinheil three-prism spectrograph and a photomultiplier.

The system was calibrated by using the emission of the positive crater of a carbon arc whose image was formed at the position of the hollow cathode by means of mirror optics. The intensities measured are therefore absolute values. The investigated spectral lines were those of the singlet system $n^1D_2 \to 2^1P_1$ as well as those of the triplet system $n^3D \to 2^3P$, both of which are within the visible range.

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Calculation of intensities

A calculation of the intensity values can be done on the basis of the following simple model: It is assumed that the atoms — at first only those of the carrier gas [6] — are excited by electron impact (excitation by photons can be completely neglected [7]), and that excitation occurs only from the ground state. Nonradiative de-excitation may also be neglected, i.e. it is assumed that de-excitation is always connected with the emission of a photon. With these limitations it is now possible to calculate the intensity of a line, i.e. its excitation rate, from the excitation cross section.

We thus arrive at the following equation:

$$I = \frac{h\nu}{4\pi} n_e n_0 l \int_0^\infty q(v_e) v_e f(v_e) dv_e; \qquad (1)$$

I = intensity of a line in erg/cm² sec sr,
n_e = electron density,
n_0 = density of gas atoms; $n_0 = p/kT_g$,
T_g = gas temperature,
l = thickness of layer,

v_e = electron velocity,
$q(v_e)$ = excitation cross section,
$f(v_e)$ = electron velocity distribution function, normalised to 1,
ν = frequency of the spectral line in $\sec^{-1}$.

Both by spectroscopic measurements [5] as well as from probe measurements [2] two values were found for n_e namely $\mathrm{Ca} \cdot 10^{10}\ \mathrm{cm}^{-3}$ and $10^{13}\ \mathrm{cm}^{-3}$. We thus have two electron groups [7]. In our case only the density of the group with the higher energy ($n_e = 10^{10}\ \mathrm{cm}^{-3}$) is of any importance, because it is this group which accomplishes excitation and ionization of the gas. The cross section for excitation can be taken from the literature [8].

By using a Maxwellian distribution for the electron velocity distribution function $f(v_e)$, we can now calculate the intensity of a spectral line. With $v_e = \sqrt{2E/m_e}$ (m_e = electron mass), $\nu = c/\lambda$ and the Maxwellian distribution function for the electron velocity of the form

$$f(E)dE = \frac{2}{\sqrt{\pi}} \sqrt{\frac{E}{(kT)^3}}\, e^{-E/kT} dE; \qquad (2)$$

we get, besides some terms which can be determined experimentally, an expression which contains an integral of the form

$$\int_0^\infty q(E) E e^{-E/T_e} dE;$$

(T_e in eV is equivalent to kT in erg). To solve this integral we form a sum of subintegrals:

$$\int_0^\infty q(E) E e^{-E/T_e} dE = \sum_{n=0}^{N} \int_{E_n}^{E_{n+1}} q(E) E e^{-E/T_e} dE. \qquad (3)$$

The values of E_n are now to be chosen in a way which permits a linear interpolation for $q(E)$ with sufficient accuracy:

$$q(E) \approx q(E_n) + \frac{E-E_n}{E_{n+1}-E_n} [q(E_{n+1}) - q(E_n)]; \qquad (4)$$

Introducing the abbreviations $E_{n+1} - E_n = \Delta E_n$ and $q(E_{n+1}) - q(E_n) = \Delta q(E_n)$ the following expression for $q(E)$ is obtained:

$$q(E) \approx q(E_n) + \frac{E-E_n}{\Delta E_n} \Delta q(E_n). \qquad (4')$$

With this interpolation the subintegrals can be solved exactly, and from equation (3) it follows that:

$$\int_0^\infty q(E) E e^{-E/T_e} dE = T_e \sum_{n=0}^{N} \Big\{ e^{-E_n/T_e} [q(E_n)(E_n + T_e) + \frac{\Delta q(E_n)}{\Delta E_n} (E_n + 2T_e) T_e] - e^{-E_{n+1}/T_e} \qquad (5)$$
$$\times [q(E_{n+1})(E_{n+1} + T_e) + \frac{\Delta q(E_n)}{\Delta E_n} (E_{n+1} + 2T_e) T_e] \Big\}.$$

The calculated intensity I_{cal} therefore is

$$I = n_e n_0 l \frac{3.74 \cdot 10^{-2}}{\lambda} T_e^{1/2} \sum_{n=0}^{N} \frac{\Delta q(E_n)}{\Delta E_n} \qquad (6)$$
$$\times [e^{-E_n/T_e}(E_n + 2T_e) - e^{-E_{n+1}/T_e}(E_{n+1} + 2T_e)].$$

In Table the investigated spectral lines and the relevant transitions as well as the measured and calculated value of the intensities are given.

Comparison of measured and calculated values of intensities of distinct spectral lines

λ (Å)	Transition	Intensity (measured)	Intensity (calculated, Maxwell)	Intensity (calculated, Druyvesteyn)
6678	$3^1D_2 \to 2^1P_1$	10 800	8800	9500
4922	4	1 320	4950	4230
4388	5	206	2640	1870
4144	6	41.7	1510	530
5876	$3^3D \to 2^3P$	12 700	5360	7250
4471	4	2 860	3920	3380
4026	5	539	1930	960

Inserting an electron velocity distribution according to Druyvesteyn in place of a Maxwellian distribution of the following form

$$f(E)dE = 1.039 \sqrt{\frac{2E}{(kT)^3}}\, e^{-0.548(E/kT)^2} dE \qquad (7)$$

the intensity values can be calculated similarly as with equation (6). The only change in equation (6) is the replacement of the factor $\exp(-E_n/kT)$ by $\exp(-0.548(E/kT)^2)$. The results of this calculation are listed in column 5 of Table.

Discussion

From Table it can be seen that for the transition with $n = 3$ the measured intensity value exceeds the calculated values; this is particularly pronounced in the triplet system. As n increases, the ratio changes and the calculated values now become higher than the measured ones. Note that the difference between measured and calculated intensities is smaller with the triplet system.

To explain the observed difference between measured and calculated intensities it is necessary to investigate the population densities and the velocity distributions more closely. The question arises whether the assumption of a population density according to Saha and a velocity distribution of electrons according to Maxwell is justified.

With most spectroscopic measurements done experimentally, e.g. temperature measurements, it is common practice to use Saha- and Maxwell expressions if local thermal equilibrium (LTE) is established. If not, the calculations are usually still done using a Maxwellian velocity distribution and the assumption is made that the population density, at least for the higher excited levels [9], will be that according to Saha. In doing so, it is, however, assumed that

(a) the electrons are thermalized,

(b) the plasma is spatially extended, i.e. no electrons can leave the energetic side of the Maxwell distribution before a sufficient number of ionizing and exciting collisions have occurred.

A velocity distribution according to Druyvesteyn, is, however, valid if electrons are introduced into the plasma on the one side and leave it on the other side before a number of collisions has been sufficient to cause a Maxwell distribution. With a Druyvesteyn distribution the number of electrons with high energies is therefore much lower, while there are much more electrons with lower and intermediate energies than with a Maxwell distribution (Fig. 1).

This now indicates — of course under the assumption that excitation occurs exclusively by electron impact and only from the ground state — that with a distribution according to Druyvesteyn the higher levels of the term ladder are less densely occupied.

In trying to explain the large difference between measured and calculated intensity values we must consider some other limitations of our model: Firstly, step excitation and step ionization: The possibility of electrons of some excited atoms being transferred into higher energy levels or separated completely from the atom before they can emit energy in the form of a photon, must be considered.

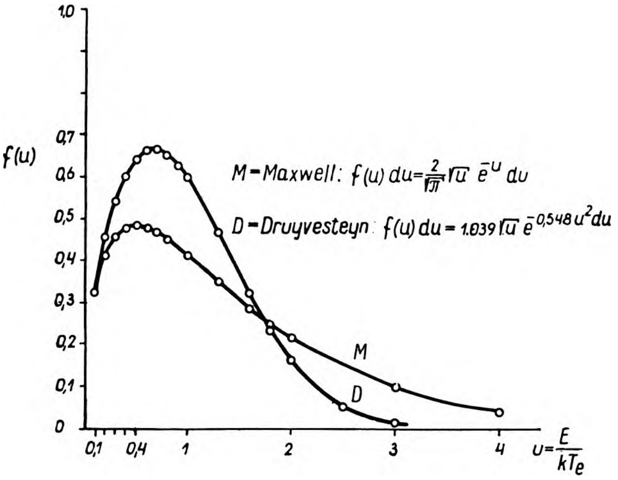

Fig. 1. Comparison of the Maxwell- and the Druyvesteyn distribution functions of the electrons

The probability for this event will, however, be negligible at the given pressure of 1 Tr. Furthermore, no provision is made for the existence of nonradiative transitions, the number of which increases with increasing main quantum number. These limitations, however, do not explain the observed difference between the triplet and singlet systems.

One has to consider that in the case of the triplet state — both spin directions parallel — excitation with sufficient probability appears only if the colliding electron changes place with an electron (of the atom) which has opposite spin. Because of this stronger interaction it takes a certain time for this exchange to take place and it is thus only possible if the kinetic energy of the colliding electron is not too high. Therefore, the function describing the excitation cross section of triplet lines drops very rapidly once the maximum excitation probability at an electron energy of about 27 eV is passed. The singlet lines, on the other hand, have a maximum excitation probability at an electron energy of about 40 eV. The decrease of the excitation function is appreciably less steep than that of the triplet lines.

Considering what has been said, the domination of the triplet system over the singlet system can now be understood from a change from a Maxwellian to a Druyvesteyn distribution. The excitation function for triplet lines will increase with the number of electrons possessing intermediate energies, while the function for singlet lines will decrease. The large difference between measured and calculated intensity values can be explained in the same way.

Another important problem is connected with the population density. Drawin [10] was the first to point out that diffusion of neutral particles into the plasma column might also be of importance. Material atoms sputtered from the cathode [11] penetrate the negative glow of the hollow cathode discharge. Due to diffusion, there will always be neutral

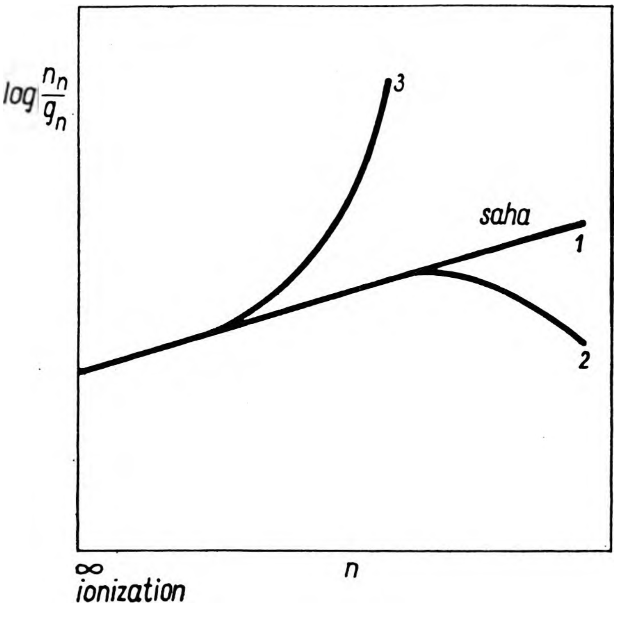

Fig. 2. The behaviour of the population density depending on the main quantum number

Curve 1: local thermal equilibrium (LTE); Saha
Curve 2: non – LTF, stationary
Curve 3: non – LTE, stationary, diffusion of neutral particles

carrier gas atoms in the glow region, especially if we consider that a continuous gas flow of about 1 ml/hr is necessary to maintain a certain pressure. Figure 2 shows the influence of this diffusion process upon the population density. Curve 1 describes a plasma in LTE, i.e. with a population density according to Saha; curve 2 is valid for the stationary non-thermal equilibrium and provides a basis for the calculations given above. Curve 3 is obtained if the stationary non-thermal plasma is subject to a diffusion stream of neutral particles.

The fundamental difference between curve 2 and 3 can be seen in the population density for small main quantum numbers. While with curve 2 the terms for small quantum numbers are underpopulated, reaching a population according to Saha with $n = 4$, we have a distinct overpopulation with curve 3, which changes to a Saha population only from $n = 10$.

Because the plasma of a hollow cathode discharge is always subject to a diffusion stream, the levels with lower main quantum numbers are overpopulated instead of being underpopulated as they are considered to be in our assumptions (curve 2). This can be taken as an explanation of the fact that the measured intensity values of the relevant transitions are relatively high, in spite of losses caused by nonradiative transitions, and of the fact that the intensity values drop very sharply with increasing main quantum number.

Conclusion

An explanation of the large difference between measured and calculated intensity values – especially at higher main quantum numbers – can be summarized as follows:

1. An electron velocity distribution according to Maxwell is not valid, since the number of collisions is too small. A better description is given by a distribution according to Druyvesteyn. Using this function the calculated intensity values are smaller, and the triplet intensities are higher than that of singlet system.

2. Nonradiative transitions – especially at levels with high main quantum numbers – cause losses when measuring intensity values. Step excitation and step ionization can be neglected.

3. The population density is influenced by a diffusion of neutral particles into the plasma which causes an overpopulation of levels with smaller main quantum numbers. The measured values of intensities of transitions with smaller main quantum numbers are thus higher than the calculated ones.

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Comparaison entre les intensités spectrales calculées et celles qu'on a mesurées au moyen du tube à cathode concave

On a comparé les intensités des singulets $n^1 D_2 - 2^1 P_1$ et des triplets $n^3 D - 2^3 P$ du He-I avec les intensités mesurées au moyen du tube à cathode concave en appliquant différentes fonctions de distribution et en admettant qu'ont lieu seulement l'excitation du niveau fondamental par collision des électrons et l'émission provoquée par le rayonnement.

Les résultats présentés montrent qu'on peut obtenir une meilleure coïncidence des valeurs calculées et mesurées quand on applique la distribution des vitesses des électrons de Druvestey et non celle de Maxwell.

L'inconvénient le plus important du modèle utilisé consiste en ceci qu'il ne tient pas compte de la diffusion des particules neutres dans le plasma.

Сопоставление спектральной интенсивности, вычисленной путём измерения при помощи лампы с полым катодом

Принимая, что возбуждение происходит исключительно с основного уровня путём столкновения электронов и что эмиссия, вызванная воздействием излучения, а также применяя разные функции разложений сопоставляются интенсивности прохождения типа $(n^1D_2—2^1P_1)$ и $(n^3D—2^3P)$ для He-I с интенсивностью, измеряемой при помощи лампы с полым катодом.

Приведенные результаты показывают, что можно получить значительно лучшее соответствие между вычисленными и измеренными величинами, если применить распределение скоростей электронов Друвестея вместо Максвелла.

Наибольшим недостатком применяемой модели является то, что она не учитывает рассеяния нейтральных частиц в плазме.

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